

AD-755 406

Glass Ocular Laser Protective Filters

American Optical Corp.

**prepared for
School of Aerospace Medicine**

OCTOBER 1972

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AD 755406

GLASS OCULAR LASER PROTECTIVE FILTERS

RICHARD F. WOODCOCK, Ph.D.



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Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract, and Indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) American Optical Corporation Research Division Southbridge, MA 01550		2a. REPORT SECURITY CLASSIFICATION Unclassified
		2b. GROUP N/A
3. REPORT TITLE GLASS OCULAR LASER PROTECTIVE FILTERS		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Final Report, 1 April 1971 - 1 August 1972		
5. AU (HORIS) (First name, middle initial, last name) Richard F. Woodcock		
6. REPORT DATE October 1972	7a. TOTAL NO. OF PAGES 29	7b. NO. OF REFS 2
8a. CONTRACT OR GRANT NO. F41609-71-C-0017	9a. ORIGINATOR'S REPORT NUMBER(S) TR-619-F	
b. PROJECT NO. 7784	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
c. Work Unit 77840013	d.	
10. DISTRIBUTION STATEMENT Approved for public release; distribution unlimited		
11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY USAF School of Aerospace Medicine Air Force Systems Command Brooks AFB, Texas 78235	
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The 0.694 μm requirement was deleted following a review of the above research program. Melt conditions and composition were finalized for 5-7 kg sized melts and enough melts were made to fabricate 50 pairs of spectacles and 10 plates (6" x 6") from this material. The spectacles had an optical density greater than 4 at the desired wavelengths and a luminous transmittance greater than 60%.		

DD FORM 1 NOV 68 1473

Ia

UNCLASSIFIED

Security Classification

UNCLASSIFIED

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Lasers						
Eye Protection, Laser						
Glass						
Spectacles						
Filter, Ocular						

Ib

UNCLASSIFIED

Security Classification

GLASS OCULAR LASER PROTECTIVE FILTERS

RICHARD F. WOODCOCK, Ph.D.
American Optical Corporation
Research Division
Southbridge, Massachusetts, 01550

USAF School of Aerospace Medicine
Aerospace Medical Division (AFSC)
Brooks Air Force Base, Texas

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FOREWORD

This report was prepared by American Optical Corporation, Research Division, Southbridge, Massachusetts. Contract Monitor was Captain Peter C. Laudieri, USAF School of Aerospace Medicine, Brooks AFB, Texas. The report covers efforts performed beginning 1 April 1971 and concluding 1 August 1972 under Air Force Contract No. F41609-71-C-0017.

ABSTRACT

This report describes a research study, the ideal goal of which, is, a filter material with an optical density of 4 or greater at 0.694, 1 to 6, and 6 to 10.6 μm , but maintaining a luminous transmittance of 50% or better. Prime emphasis was placed on meeting or exceeding the luminous transmittance requirement wherein lies the major benefits as well as the major technical problems. The research included an investigation of the effect on spectral properties of glass compositions prepared with CuO, FeO, rare-earth oxides, various "host" glass ingredients and various melt conditions; either singly or in combination.

The 0.694 μm requirement was deleted following a review of the above research program. Melt conditions and composition were finalized for 5-7 kg sized melts and enough melts were made to fabricate 50 pairs of spectacles and 10 plates (6" x 6") from this material. The spectacles had an optical density greater than 4 at the desired wavelengths and a luminous transmittance greater than 60%.

GLASS OCULAR LASER PROTECTIVE FILTER

I. INTRODUCTION

With the advent of increasing numbers of laser systems operating in the infrared region between the 1.06 μm emission wavelength of neodymium systems and the 10.6 μm wavelength of CO_2 systems, the need for protection in this region becomes increasingly desirable. The goal of the present work was to carry out a research and development program in an effort to produce an ocular filter with the following characteristics to meet these needs:

The filter should possess an optical density greater than 4.0 at 0.694 μm , at all wavelengths from 1 μm through 6 μm and at all wavelengths from 6 μm through 10.6 μm if feasible and should attempt to have a luminous transmittance of 50% or better. The material should provide this protection at all angles of incidence of the incoming light. The configuration of the final hardware item is to be a spectacle goggle which is lightweight. (The AO series F-9900 frame was deemed suitable for this purpose by the contracting agency).

Items to be delivered under the contract consist of 50 spectacle goggles and 10 samples of the developed material in the form of 6 x 6-inch plates.

The program for accomplishing these goals consisted of: (1) a research program on glass composition to provide the desired spectral characteristics; (2) selection of the best composition midway through the contract for use in the final hardware items; (3) scaling up the melting procedure of this optimal composition from small experimental 100-200 g melts to 5-7 kg "production" melts, and (4) fabrication of the hardware items from these production melts.

Composition investigations during the first six months consisted of three concurrent studies, namely; (1) a single glass composition containing both Cu^{2+} -ions (for protection at 0.694 μm) and Fe^{2+} -ions (for protection in the region beyond 1 μm), (2) the optimization of two glass compositions, one containing Cu^{2+} -ions and the other containing Fe^{2+} -ions, which could be laminated together to form the desired hardware items and (3) compositions containing other "colorants" such as rare-earth ions or radicals to provide protection at the transmission peaks in the 1 to 10.6 μm region so that the amount of iron oxide might be reduced.

A contract conference took place at American Optical Corporation in early November 1971 to finalize the glass composition and the specifications of the hardware items to be delivered. At this meeting, it was suggested by the contracting agency that a modification in the hardware specifications might be made which would delete the requirement for protection at 0.694 μm . The project was reevaluated with the possibility of this contract modification in mind. If this deletion was to be made it appeared that the best approach would be to increase the FeO concentration to provide absorption at the 2.75 μm peak and maintain a moderately high level of absorbed water in the glass to provide absorption at the 3.75 μm peak.

Official notice of a contract modification to delete the 0.694 μm requirement was received in February. A four-month, "no cost" time extension was requested and received to allow time to scale up the melt size, prepare several of these larger melts to supply raw material for the hardware items, and fabricate the desired hardware items since there was not sufficient time to complete the remaining tasks before the original contract termination date.

In summary, the first half of the contract effort involved an investigation of phosphate-based glasses containing FeO, CuO, rare-earth oxides, and absorbed gases and melted under a variety of oxidation-reduction conditions in an attempt to develop a filter material with an optical density greater than 4 at wavelengths of 0.694 μm and from 1 to 10.6 μm with a luminous transmittance of 50% or better. Following the deletion of the 0.694 μm requirement the results of the above investigation were reevaluated, a composition for the filter material was chosen, the melts were scaled up to 5-7 kg sized melts and raw material was produced for the desired deliverable items.

The spectacle goggles delivered under this contract have an optical density greater than 4.0 in the spectral region from 1 to 10.6 μm as specified in Modification No. P00001 of the contract. This was attained by using a phosphate-based glass containing Fe^{2+} -ions in a lens thickness of 3.6 mm or greater. The luminous transmittance of these spectacles is 60% or better. One pair of the size 48 goggles contains lenses consisting of a laminate of the experimentally developed Fe-phosphate glass, and a commercially available Cu-phosphate glass which provides an optical density of approximately 4.0 from 0.694 μm to 10.6 μm with a luminous transmittance of about 35%. The single element lenses were heat treated to make them "break resistant," in accordance with FDA regulations, but should not be considered for use as safety glasses for protection against flying objects. A photograph

of the delivered spectacles is shown in Fig. 1.



Figure 1. Photograph of spectacles. They have an optical density greater than 4.0, and luminous transmittance of about 65% for a lens thickness of 3.5-3.6 mm.

II. RESEARCH PROGRAM

The requirement for an optical density greater than 4.0 in the 6 to 10.6 μm region is easily satisfied because conventional glasses are composed of oxides and the vibrational absorption frequency of the cation-oxygen pair has its fundamental frequency near the long wavelength end of this region. The extremely high absorption at the fundamental wavelength creates a very broad and strong absorption band which encompasses the whole 6 to 10.6 μm region.

Protection at the 0.694 μm wavelength can be supplied by the addition of Cu^{2+} -ions to the glass. A material containing just Cu^{2+} -ions, however, will not provide adequate protection

beyond about $1.3 \mu\text{m}$ as shown in Fig. 2. It will, therefore, be necessary to include Fe^{2+} -ions in the final filter, either in addition to the Cu^{2+} -ions in a single component filter or in a second component of a composite filter. An anticipated problem for copper-containing glasses is the poor transmission in the visible region, i.e., the luminous transmittance of the best available commercial copper-containing glass is about 45% for a sample with an optical density of 4.0. The best visual transmittance for both copper- and iron-containing glasses is obtained when the base glass is a phosphate-type material. For this reason, only phosphate-based glasses were considered in this program.

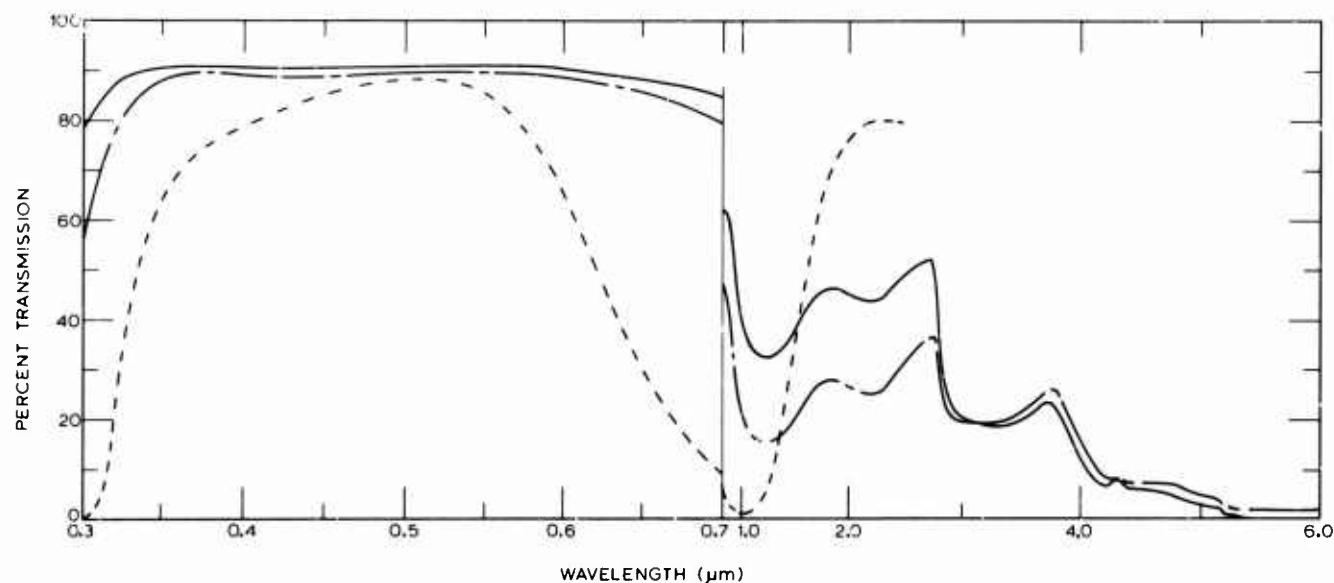


Figure 2. Spectra of existing Cu-phosphate and Fe-phosphate glasses. Nominal sample thickness 0.5 mm. Schott BG-18 (---), Pittsburgh Plate Glass N-2043 (—), and Schott KG-3 (— · -). Note change in wavelength scale.

The best protection in the 1 to $6 \mu\text{m}$ region of the spectrum for a filter material with optimum luminous transmittance is obtained with phosphate-based glasses containing Fe^{2+} -ions. Problems anticipated in these materials are associated with transmission peaks in the 1 to $6 \mu\text{m}$ region as shown in Fig. 2. All of the samples in Fig. 2 are a nominal 0.5 mm in thickness. Extrapolating data from this sample thickness indicates that transmission

should not exceed 24.5% in an 0.5 mm thick sample if an optical density of 4 is to be maintained for a sample thickness of 3.5 mm or 28% for a 4 mm sample. A transmission of 40% would require a sample thickness of 5.6 mm in order to obtain an optical density of 4, and a transmission of 50% would require a sample thickness of 7.7 mm. The best material in the 1 to 6 μm region in Fig. 2, KG-3, would require a thickness of about 5 mm for an optical density greater than 4.0 and would not be considered to be "lightweight."

The initial approach to the overall experimental program was divided into the following subtasks: (1) develop a copper-iron phosphate or an iron-phosphate glass composition with maximum luminous transmittance, the latter for use with existing copper-phosphate materials which are known to have marginal luminous transmittance, (2) correlate the transmission peaks in the 1 to 6 μm region of these glasses with glass composition and try to adjust composition so that an optical density of 4 can be achieved in a suitable sample thickness, and (3) scaling up the melt size from experimental to production.

The study to optimize the glass composition was to be carried out in small experimental melts weighing 100-200 grams. After the composition of the filter glass had been finalized, techniques would be devised for melting this composition in larger (5 kg) sized melts. In the larger sized melts the equilibrium oxidation-reduction conditions and concentrations of dissolved gasses may be significantly different from the smaller experimental melts. It is, therefore, necessary to adjust the melting conditions to reproduce the spectral characteristics of the smaller melts.

Adjusting the composition to provide an optical density greater than 4.0 in the 1 to 6 μm region in a suitable lens thickness may require one or more of the following approaches: (1) increase the total FeO concentration, (2) increase the Fe^{2+} -ion concentration by modifying host glass composition, the reducing conditions of the melt, or both, (3) modify the host glass composition to shift the long wavelength cutoff to a shorter wavelength, and (4) the addition of rare-earth oxides or absorbed gasses as colorants to provide additional absorption bands within this region. Conventional safety glasses, which are not uncomfortable to the wearer, have a lens thickness of 3.2-3.4 mm; therefore, this thickness was chosen as a goal for the present work.

III. COPPER-CONTAINING GLASSES

A series of phosphate-based glasses were made containing copper, iron, and a combination of copper and iron to investigate

the possibility of combining all of the desired spectral characteristics in a single glass composition. The compositions investigated include those which give the best spectral results for copper-phosphate and iron-phosphate filter materials. Some of these compositions were remelted several times using different atmospheric conditions in the furnace during the melting process. These compositions and spectral results are listed in Table I.

Based on the transmission properties of the singly doped glasses containing just copper (OLF-5) and just iron (OLF-4) as a colorant one can calculate the expected spectral characteristics for the glass OLF-6 which contains both copper and iron in its composition. When this is done one finds for glasses melted in a normal atmosphere that; (1) transmission at 410 nm should be approximately 60% (the transmission at 410 μm of OLF-4 multiplied by the transmission at 410 μm of OLF-5 taking the Fresnel reflectance of two rather than four surfaces into consideration) whereas the actual transmission of OLF-6 at this wavelength is only 12%, (2) maximum transmission in the visible region (500-600 nm) should be approximately 80% compared to 53.5% for the actual glass, (3) transmission at 694 nm should be approximately 16% compared to 21% in the actual glass, and (4) transmission at 1.06 μm should be 3.5% compared to 8.5% in the actual glass. Similar results are indicated in Table I for other atmospheric conditions.

It would appear from these data that a couple is formed between the Cu-ion and the Fe-ion which shifts the valence of the copper from Cu^{2+} to Cu^{1+} and the valence of the iron from Fe^{2+} to the Fe^{3+} , i.e., the transmission at 410 nm is significantly decreased which indicates that the iron has been shifted toward the Fe^{3+} valence and the transmission at 694 nm is somewhat increased indicating a decrease in copper in the Cu^{2+} valence. Attempts to adjust the equilibrium ratios of these two colorants by varying the oxidation and reduction conditions of the melt (OLF-6A through OLF-6E) were unsuccessful as is shown by the results in Table I. Varying the composition of the host glass also appears to be relatively ineffective as a means of modifying this couple and its resulting spectral characteristics. It may be noted that a significant decrease in transmission at 5.0 μm is observed when B_2O_3 is present in the glass composition.

These results suggest that for the double doped glass a compromise will be required between the spectra of the best Cu-phosphate glass and the best Fe-phosphate glass and thus an even greater compromise between the specification of an optical density of 4 at the wavelengths desired and the attempt to maintain luminous transmittance at 50% or better. These results would strongly suggest the use of the laminated filter.

Table I. Spectral characteristics of phosphate glass composition containing iron and copper as colorants.

Melt Number	Compositions (mol%)						Melt Conditions	Transmission (%) at Specific Wavelengths (μm)									
	Li ₂ O	Na ₂ O	BaO	ZnO	B ₂ O ₃	Al ₂ O ₃		P ₂ O ₅	CuO	FeO	0.410	Max.	0.694	1.06	2.2	2.7	5.0
OLF-6	14	-	-	-	-	19	57	5	5	-	12	53	21	8	5	53	64
OLF-6A	14	-	-	-	-	19	57	5	5	N ₂	13	54	20	7	54	64	
OLF-6B	14	-	-	-	-	19	57	5	5	N ₂ , Reducing	11	53	22	8	52	63	
OLF-6C	14	-	-	-	-	19	57	5	5	N ₂ , Low Temp.	14	57	30	12	47	57	
OLF-6D	14	-	-	-	-	19	57	5	5	N ₂ , High Temp.	11	53	22	9	52	63	
OLF-6E	14	-	-	-	-	19	57	5	5	Cl Added	12	50	25	12	56	68	
OLF-18	-	-	-	-	-	14.2	19	56.8	5	-	5	42	32	11	35	48	
OLF-21	-	11.7	2.5	4.5	5.8	12.7	52.8	5	5	-	11.5	58	14	3	60	48	
OLF-23	-	-	-	-	-	22.5	67.5	5	5	N ₂	18	55.8	38	12	37	47	
OLF-42	-	-	-	6	-	23	61	5	5	N ₂	15	57	48	15	38	50	
OLF-5	15	-	-	-	-	20	60	5	-	-	77	88	17	6	84	86	
OLF-5A	15	-	-	-	-	20	60	5	-	N ₂	74	87	18	6	84	85	
OLF-5B	15	-	-	-	-	20	60	5	-	Cl Added	57	81	47	29	87	86	
OLF-4	15	-	-	-	-	20	60	-	5	-	71	82	82	49	55	63	
OLF-4A	15	-	-	-	-	20	60	-	5	N ₂	73	82	82	41	48	58	
OLF-4D	15	-	-	-	-	20	60	-	5	N ₂ , Reducing	80	85	83	33	43	52	
OLF-1	-	-	-	-	-	24	65	-	5	-	82	86	79	22	28	40	

Some effort was made to provide absorption in the IR-region of these materials by varying the absorbed gas content of the glass and by the addition of rare-earth ions to the glass. The success and problems encountered with these approaches will be discussed separately since they also apply to glasses containing just FeO.

Effect of Host Glass on IR Transmission

Transmission measurements were made in the infrared on a series of phosphate-based glass compositions which had been melted prior to this contract for other purposes. This series of 21 compositions, which included most of the glass ingredients used in the preparation of phosphate glass compositions, contained Li_2O , Na_2O , K_2O , Rb_2O , CaO , BaO , ZnO , MgO , ZrO_2 , B_2O_3 , La_2O_3 , P_2O_5 , Y_2O_3 and SiO_2 . Some of these glasses contained no colorant and others contained CuO .

The results of this study, in general, agree with the results listed in Table I which indicates that the principal effect of host composition is a decrease in transmission in the 4.0 to 5.0 μm region when B_2O_3 is added to the glass composition. The only other observable difference is the variation in the water absorption band in the 2.75 to 4.0 μm region which is probably affected more by melt conditions than the glass composition. Although there is a transmission peak in the 5 μm region, this does not appear to be a limiting factor in obtaining optical density of 4 throughout the IR, even for glass compositions which contain no B_2O_3 .

Rare-Earth Absorption Bands in the Near Infrared

The best infrared absorbing glass compositions consist of Fe^{2+} -ions in a phosphate-based material. Even these compositions, however, have transmission windows occurring at approximately 1.8-2.0 μm , 2.75 μm , 3.75 μm and 5.0 μm . None of the other transition metal ions provide absorption in these regions, therefore the narrower band rare-earth ions were investigated for this purpose. Transmission spectra were measured on phosphate glasses containing Pr_2O_3 , Dy_2O_3 , Eu_2O_3 , CeO_2 , Tb_2O_3 , Sm_2O_3 and Er_2O_3 . These rare-earth ions were chosen based on their energy level diagrams in a crystalline host which give the position of the absorption band but not the shape or intensity of the band, all of which may differ slightly in a glass host in any case.

To investigate the effect of rare-earth ions on the Cu^{2+} -ion spectra, a series of glasses (OLF-25, 26, and 27) was made, based on the copper-containing OLF-5 composition, to which Pr^{3+} -,

Sm^{3+} -, and Eu^{3+} -ions were added, respectively. As shown in Fig. 3, combining rare-earth ions with Cu^{2+} -ions appears to have little adverse effect on the spectrum of the latter. A similar series of glasses (OLF-28, 29, and 30) was made based on the iron-containing OLF-1 composition. Spectra of one of these glasses (OLF-29) together with an OLF-1 glass are shown in Fig. 4. A comparison of the absorption band at $1.06 \mu\text{m}$ (Fe^{2+} -ions) and $0.410 \mu\text{m}$ (Fe^{3+} -ions) indicates that the presence of rare-earth oxides in the glass has the adverse effect of shifting the iron valence toward the Fe^{3+} . The curve for OLF-29A shows the result of one of the attempts to shift the iron toward the Fe^{2+} valence by increasing the reducing condition in the melt (to be discussed later).

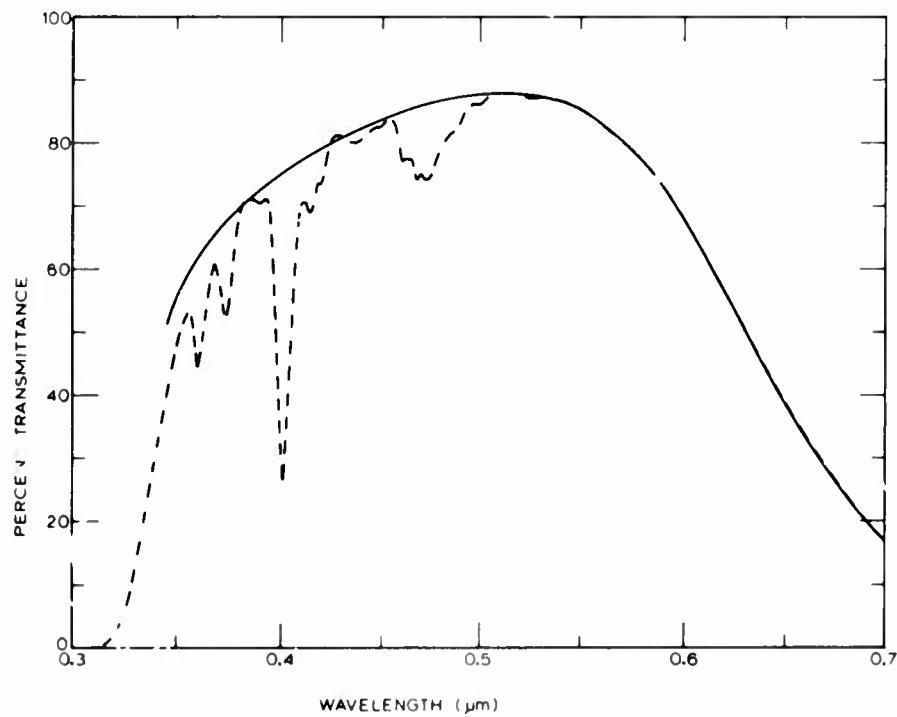


Figure 3. Effect of rare-earth ions on Cu-glass spectra. Transmission of OLF-5 (—) containing Cu^{2+} -ions and OLF-6 (---) containing Cu^{2+} -ions and Sm^{3+} -ions. Nominal sample thickness 0.5 mm.

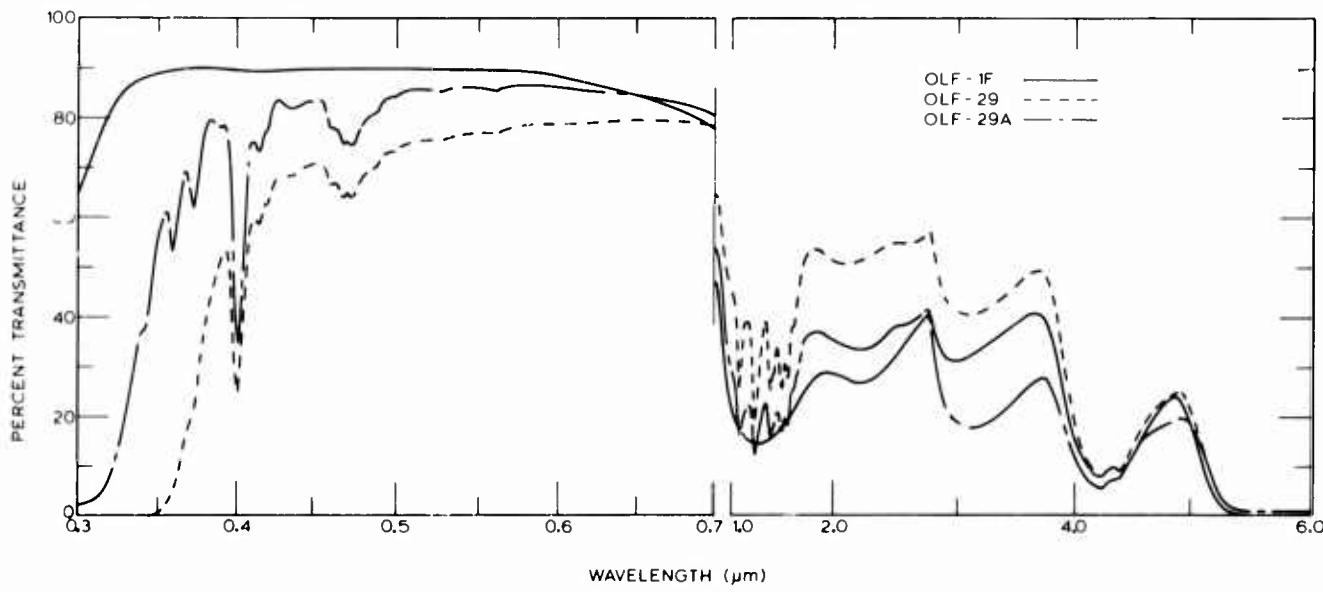


Figure 4. Effect of rare-earth ions on Fe-glass spectra. Transmission of OLF-1F containing FeO melted in N₂ atmosphere with 1.5 wt% sugar in the batch to enhance reducing conditions (—), OLF-29 containing FeO and SmO melted in N₂ atmosphere (----), and OLF-29A melted in N₂ atmosphere with 3.0 wt% sugar in the batch (—). Nominal sample thickness 0.5 mm; uncorrected for Fresnel loss.

These results indicate that the rare-earth should be added just to the copper glass component of a laminated filter. In order to get maximum benefit from the rare-earth ions it would be desirable to have the maximum amount of rare-earth ion in all components of the final filter. Some effort was, therefore, made to shift the Fe²⁺ - vs Fe³⁺-ion ratio more towards the Fe²⁺ valence in the Fe-phosphate glasses containing rare-earths. Since the rare-earth oxides (R₂O₃) as glass components tend to behave in a manner similar to aluminum oxide (Al₂O₃), a series of glasses was made in which the rare-earth oxide (Pr₂O₃) was substituted on a mol % basis for Al₂O₃ in glass composition OLF-38 which has relatively good Fe³⁺ spectral characteristics.

Results of this study are shown in Table II, together with transmission data for a glass containing just Pr₂O₃ (OLF-33) and the parent glass containing just FeO (OLF-38) for comparison. The transmission spectra of OLF-33 indicate that the Pr³⁺-ion alone has no affect on the transmission in the 0.41 and 1.06 μm

Table II. Effect of Al_2O_3 vs Pr_2O_3 on transmission spectra of Fe-glasses.

Melt No.	Oxide composition (Mol%)				Transmission (%) vs wavelength (μm)					Thickness (mm)			
	ZnO	Al_2O_3	P_2O_5	FeO	Pr_2O_3	0.410	Max.	1.06	2.0	2.75	3.75	5.0	
OLF-33	11.3	3.6	79	-	5.8	89.5	90	83	17	86	50	19	0.52
OLF-38	6	24	65	5	-	87	89	25	35	45	33	23	0.49
OLF-43	6	14	65	5	10	68	80.5	50.5	22	66	37	21	0.52
OLF-44	6	9	65	5	15	63	80	53	14	70	43	18	0.53
OLF-45	6	4	65	5	20	60	77.5	46	10.5	66	45	18	0.48

regions. When Pr_2O_3 is substituted for Al_2O_3 in the OLF-38 composition, however, the transmission at $0.41 \mu\text{m}$ decreases and the absorption at $1.06 \mu\text{m}$ decreased indicating a shift from Fe^{2+} -ions to Fe^{3+} -ions in both cases.

The most encouraging results were obtained when one of these glasses, OLF-43, was remelted with various changes in the melt condition to provide a more reducing atmosphere. These results are given in Table III. The ratio of the transmission at $0.410 \mu\text{m}$ (T_{410}) vs the maximum transmission value obtained in the visible region (T_{\max}) is given as an indication of the relative amount of Fe^{3+} -ion present in the glass. As indicated in the table, good results are obtained when the praseodymium is added as a phosphate compound rather than as an oxide and with the glass melted under a nitrogen atmosphere. The melt in which the praseodymium is added as the oxide but with a reducing agent added to the glass composition also shows substantial improvement over the original melt. These original experiments were carried out using Pr_2O_3 because this rare-earth oxide is relatively inexpensive and provides absorption in the $3.75 \mu\text{m}$ region (cf. Fig. 5).

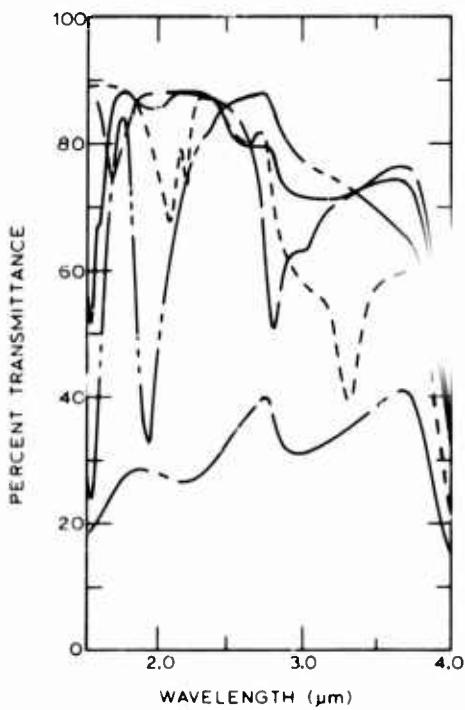


Figure 5. Spectra of rare-earth doped glasses in the near infrared. Dy^{3+} -phosphate glass (---), Sm^{3+} -phosphate glass (—), Eu^{3+} -phosphate glass (— · —), Pr^{3+} -phosphate glass (— · · —), plus Fe^{2+} -phosphate glass (— · · · —) to show position and shape of IR peaks where additional absorption is required. Nominal sample thickness 0.5 mm.

Table III. Effect of melt conditions on the Fe-spectrum of glasses containing rare-earths.

Melt Number	Melt Conditions	Transmission (%) vs λ (μm)			T_{410}/T_{max}	Thickness (mm)
		0.410	Max.	1.06		
OLF-43	Pr as Pr_6O_{11} , N_2 atmosphere	68.0	80.5	50.5	0.85	0.52
OLF-43A	Pr as PrPO_4 , N_2 atmosphere	85.2	87.2	25.0	0.98	0.51
OLF-43B	Pr as Pr_6O_{11} , reducing agent, N_2 atmosphere	79.0	83.2	25.5	0.95	0.53

Transmission curves of the more promising rare-earth glasses providing protection at 2.75 μm and 3.75 μm are shown in Fig. 5 together with a typical Fe-phosphate glass to indicate the position and general shape of the transmission peaks where additional absorption is required. Concurrent studies indicate that the absorption peak at 3.75 μm may be controlled to an acceptable level by enhancement of the water band which is centered at about 3.0 μm . This leaves the absorption peak at 2.75 μm as the limiting factor in achieving the desired optical densities throughout the IR region. Absorption at 2.75 μm is strongest for glasses containing Dy^{3+} , Sm^{3+} , Eu^{3+} , and Pr^{3+} , in that order.

Although the Dy^{3+} -ion shows the strongest absorption right at 2.75 μm , the absorption decreases rapidly as the wavelength decreases to 2.5 μm . In contrast, both the Sm^{3+} - and Eu^{3+} -ions exhibit a rather broad absorption between 2.75 and approximately 2.5 μm . In order to flatten off the 2.75 μm peak of the Fe-containing phosphate-based glass, it may be advantageous to use a combination of Dy^{3+} -ions and either Sm^{3+} - or Eu^{3+} ions. Several glasses of this type were melted. The results indicate that a glass containing Sm_2O_3 alone or in combination with a smaller concentration of Dy_2O_3 , to trim the peak at 2.75 μm , gives the best results.

The original melt of glass containing Sm_2O_3 and FeO (OLF-29) indicated the presence of a considerable amount of Fe^{3+} -ions (cf. Fig. 4). Subsequent melts of the OLF-29 composition (OLF-29A through F) were therefore melted using some of the techniques developed during the study of Pr_2O_3 glasses for the improvement of the $\text{Fe}^{2+}:\text{Fe}^{3+}$ ratio. Attempts to add the Sm^{3+} -ion in the form of a phosphate compound rather than an oxide, as was done in the case of Pr^{3+} -ions study, were severely delayed due to the difficulty in locating a rare-earth materials vendor who would supply the samarium in the form of a phosphate, and very slow delivery once the order had been placed. Results with this glass were not encouraging, but one should perhaps investigate the quality of the Sm-phosphate material obtained, based on the difficulties encountered in obtaining it.

At this point in the program, official notice was received from the Contracting Agency that the requirement for protection at the 0.694 μm wavelength had been deleted from the contract. With the deletion of the Cu^{2+} -ion requirement, which inherently has poor visual transmittance, the requirements for high visual transmittance on the Fe^{2+} -ion glass are relaxed considerably. This makes it possible to increase the FeO concentration of the glass and, in this way, decrease the transmission in the 2.5 to 2.75 μm region without lowering the transmission in the visible region of the spectrum below the 50% visual transmittance

requested in the specification. Based on this argument, very little additional work was done on rare-earth ion compositions and the remaining emphasis was placed on optimizing FeO-containing glasses and techniques for melting them in larger sizes.

IV. IRON-CONTAINING GLASSES

FeO Concentration

The initial series of iron-containing phosphate composition (OLF-1, 2 and 3) were melted to determine a rough upper limit of the amount of iron oxide that could be incorporated in a phosphate-based glass. Spectral characteristics of these glasses which had an iron concentration equivalent to 3, 7 and 10 wt% FeO are given in Table IV. For the sake of consistency, the iron concentration in the glass is always calculated as FeO although the iron is not necessarily added to the batch as FeO and probably does not exist as pure FeO (Fe^{2+} -ions) in the final glass sample.

The data given in Table IV for these three glasses which were melted in an air atmosphere, indicate that much of the iron exists as Fe^{3+} -ions at the higher FeO concentrations. The OLF-3 sample contained what appeared, by visual inspection, to be metallic inclusions. More careful examination with a microscope indicates there may also be a few iron crystals in the glass containing 7 wt% FeO. Most of the preliminary investigations were therefore carried out using 2 wt% FeO.

The concentration range between 3 and 7 wt% FeO was subsequently investigated in more detail. These compositions (OLF-47, 48 and 49) were all melted in a nitrogen atmosphere with a reducing agent added to the glass batch. A comparison of the transmission values at 0.410 μm and at maximum transmission given in Table IV, indicates that very little of the iron is present as Fe^{3+} -ions. The absorption at 1.06 μm increases with the increase in FeO concentration, but not as rapidly as Beer's Law would indicate, i.e., the extinction coefficient ($\epsilon_{1.06}$) is not constant but decreases as the FeO concentration is increased. In calculating the values of ϵ the value of the transmittance of the base glass with no iron present was assumed to be 90% and the density was assumed to be constant for the three glasses with a value of about 2.5. The decrease in ϵ with increasing FeO concentration is assumed to be due to the presence of iron in some valence other than Fe^{2+} , either as an Fe^{2+} - Fe^{3+} complex or as colloidal-free ion. Either of these forms of iron could be responsible for the gradual decrease in transmission throughout the visible region.

Table IV. Spectral characteristics as a function of FeO-concentration.

Melt Number	FeO Conc.		Transmission (%) vs λ (μm)			Thickness (mm)	$\epsilon_{1.0\text{e}}$ a
	(wt%)	(Mol%)	0.410	Max.	1.06		
OLF-1	3	5.21	82	86	22	0.52	
OLF-47	4	6.9	89.0	90.0	11.0	0.48	14.2
OLF-48	5	8.6	88.0	89.0	8.0	0.48	12.6
OLF-49	6	10.2	87.5	88.5	4.5	0.53	11.8
OLF-2	7	11.8	39.0	67.0	7.0	0.52	
OLF-3	10	16.5	40.0	65.0	2.5	0.53	

a The extinction coefficient ϵ is defined by $I=I_0 \cdot 10^{-\epsilon cd}$, where c is the concentration in gm. mol/liter and d is the thickness.

Effect of Host Glass Composition on Transmission Spectra of Fe-Glasses

A variety of glasses were made to investigate the effect of the host material on the spectral properties of Fe-phosphate glasses. These include an investigation of the effects of the addition of "network modifiers" such as alkali oxides (Li_2O through Rb_2O), which usually have the greatest effect on glass properties, and the variation of the relative amounts of "network modifier" and "network-forming" elements, i.e., ZnO vs Al_2O_3 vs P_2O_5 . Results of these studies are given in Table V.

To investigate the effect of alkali oxides a series of phosphate compositions was prepared which contained 5 mol % (approximately 3 wt%) of iron oxide and 15 mol % of the various oxides being investigated. Data in Table V indicate that the transmission characteristics of these glasses in general improves as one goes from lithium, to sodium, to potassium with the properties of the rubidium glass being about the same as those of the potassium glass. This improvement is probably due to the fact that the oxidizing conditions within the melt tend to decrease as the alkali element is changed from lithium to rubidium.

The glass system chosen to investigate the effects of network modifiers vs network-forming elements was a ZnO - Al_2O_3 - P_2O_5 composition because the initial melt of this composition (OLF-1) had relatively good spectral properties and this compositional system is known to be one of the more chemically durable phosphate-based glasses. For the series (OLF-36, 24, 32, 31) containing 60 mol % P_2O_5 , 5 mol % FeO with the remainder of this composition made up of varying concentrations of ZnO and Al_2O_3 , the results in Table V indicate that the spectral properties improve as the ZnO concentration is decreased. Attempts to melt the end member of this series containing 35 mol % Al_2O_3 and 0 mol % ZnO were unsuccessful. Some difficulties were also encountered in melting composition OLF-36, the member with the next lowest ZnO concentration. This series shows a general improvement in spectral characteristics as the ZnO concentration is decreased, i.e. an increase in the ratio of transmission at 0.410 vs maximum transmission (indicative of freedom from Fe^{3+}) and a general decrease in transmission at 1.06 μm (indicative of the presence of Fe^{2+} -ions).

Based on the best glass in the above series, OLF-36, a second series of glasses was investigated in which the ZnO : Al_2O_3 ratio was held fixed at 1:4 and the relative concentrations of P_2O_5 vs the combined concentrations of ZnO and Al_2O_3 were varied (OLF-40, 36, 38, 39 and 41). The concentration of FeO

Table V. Effect of host glass composition on spectra of Fe-glasses.

Table V. Effect of host glass composition on spectra of Fe-glasses.

Melt number	Composition (mol%)						Melt Conditions	Transmission (%) vs wavelength (μm)			T_{410}/T_{\max}	
	Li ₂ O	Na ₂ O	K ₂ O	Rb ₂ O	BaO	ZnO		Ba ₂ O ₃	Al ₂ O ₃	P ₂ O ₅	FeO	
DLF-4	15	-	-	-	-	-	60	5	-	71.0	82.5	0.86
DLF-7	-	15	-	-	-	-	60	5	N ₂ Atmos.	72.0	83.5	0.86
DLF-8	-	-	15	-	-	-	60	5	N ₂ Atmos.	74.0	84.5	0.88
DLF-9	-	-	-	15	-	-	60	5	N ₂ Atmos.	71.5	84.0	0.85
DLF-24	-	-	-	-	-	-	60	5	N ₂ Atmos.	79.0	84.0	0.94
DLF-19	-	-	-	-	-	-	60	5	N ₂ Atmos.	75.0	81.5	0.92
DLF-37	-	-	-	-	-	-	60	5	N ₂ Atmos.	87.0	88.0	0.99
DLF-36	-	-	-	-	-	-	60	5	N ₂ Atmos.	79.0	84.0	0.94
DLF-24 ^a	-	-	-	-	-	-	60	5	N ₂ Atmos.	82.0	88.0	0.93
DLF-32	-	-	-	-	-	-	60	5	N ₂ Atmos.	74.5	83.0	0.90
DLF-31	-	-	-	-	-	-	60	5	N ₂ Atmos.	87.0	89.0	0.98
DLF-40	-	-	-	-	-	-	55	5	N ₂ Atmos.	83.5	87.0	0.96
DLF-36 ^a	-	-	-	-	-	-	60	5	N ₂ Atmos.	72.5	82.0	0.88
DLF-38	-	-	-	-	-	-	65	5	N ₂ Atmos.	87.0	89.0	0.99
DLF-39	-	-	-	-	-	-	70	5	N ₂ Atmos.	87.0	88.0	0.94
DLF-41	-	-	-	-	-	-	75	5	N ₂ Atmos.	82.0	82.0	0.93
DLF-19 ^a	-	-	-	-	-	-	60	5	-	75.0	81.5	0.92
DLF-20 ^{a,b}	-	12.5	-	-	-	-	55.6	5	-	68.5	82.0	0.84
DLF-46	-	-	-	-	-	-	64.3	5	N ₂ Atmos.	90.0	90.0	1.00
DLF-51	-	-	-	-	-	-	63.2	4.9	N ₂ Atmos.	89.0	89.0	1.00
									3% sugar			

^a Repeated for ease of comparison

Second melt - first devitrified

was again held at 5 mol %. This series would have provided data for glasses with P_2O_5 concentration ranging from 55 mol % to 75 mol %, however, the 55 mol % composition did not make glass. Data on these glasses are included in Table V and indicates that the ratio of Fe^{2+} to Fe^{3+} -ions improves as the concentration of P_2O_5 is decreased.

Also included in Table V are data on a series of glasses containing B_2O_3 . The initial melts in this series, OLF-19 and 20 were made to see if B_2O_3 , which provided absorption at 5 μm for iron-free phosphate base glasses, could be combined with FeO without adversely effecting the spectral properties of either component. As indicated in Table V, the absorption for these glasses at 5 μm is still good, but the ratio of transmission at 0.41 and maximum transmission indicates the presence of Fe^{3+} -ions. The subsequent glasses, OLF-46 and 51, were melted in a nitrogen-rich atmosphere with a reducing agent added to the glass batch and cover a lower range of B_2O_3 concentrations. The latter compositions still show good absorption at 5 μm and, in addition, show little evidence of the presence of Fe^{3+} -ions.

Further work with B_2O_3 compositions was not pursued because the transmission peak at 5 μm was not considered to be the limiting factor in obtaining an optical density of 4 in the near IR region, plus the fact that it tends to be an oxidizing ingredient and requires extra effort to nullify this effect. It is conceivable that some benefit might have been realized by the addition of B_2O_5 in the 3.75 μm region if transmission at this peak had not been controlled by the addition of water vapor to the glass.

Effect of Melt Conditions on Transmission Spectra of Fe-Glasses

The composition of gasses within the melt or within the furnace during the melting process may effect the spectral properties of the resulting glass either by controlling the oxidation-reduction conditions in the melt or by controlling the concentration and type of radicals or ions within the melt (e.g., OH^- , $SO_4^{=}$).

In most of the studies on the effect of melt conditions, an attempt was made to introduce the desired conditions into the glass melt, either by varying the compounds used to introduce the cations into the melt (e.g., ZnO vs $ZnCO_3$ vs $Zn_3(PO_4)_2$ etc.) or by the addition of a "volatile" component to the glass batch composition, such as sugar to provide a form of carbon as a reducing agent plus OH^- -ions. In this way, the desired ingredient is "in the glass" right from the initial chemical reaction stage of the

melting process. In addition, the desired ingredient was sometimes present in a gas mantle above the melt in order to maintain the partial pressure above the melt surface at a high enough level to prevent volatilization of the desired ingredient during later stages of the melting process.

Oxidation-Reduction Condition: The predicted positions of absorption bands, based on Ligand field theory [1], for transition metal ions in glass agree reasonably well with experimental evidence. One of the exceptions is the case of Fe^{3+} -ion due to the complexity of its spectra and its site in the glass. Absorption bands for Fe^{3+} -ions in octahedral sites in a phosphate glass are predicted [2] at about 0.17, 0.525, and 0.732 μm based on the best computer fit of Ligand field parameters to observed absorption bands in this glass. Based on the assumption that the strength of the Ligand field in tetrahedral sites is 4/9ths the value of that of octahedral sites, one would expect absorption bands to occur at about 0.417, 0.434, and 0.494 μm for an Fe^{3+} -ion in a tetrahedral site in the same glass composition.

Figure 6 shows the absorption spectrum of a 3.65 mm sample of OLF-61K in the visible. The benefit derived from controlling the reducing conditions of the melt is the potential elimination of these absorption bands throughout the visible region due to Fe^{3+} -ions.

Although the OLF-61K composition differ slightly from that of Ref. 2, reasonably good agreement is obtained between the observed absorption bands in Fig. 6 and predicted values by assigning the absorption band at 530 μm and a broader, stronger band centered at about 415 μm to octahedral sites and the bands at about 422, 458 and 485 μm , superimposed on the long wavelength tail 415 μm band to Fe^{3+} -ions in tetrahedral sites. These data indicate that the relative number of tetrahedral sites is considerably less than octahedral sites as evidenced by the lower total absorption of ions in tetrahedral sites which are expected to have higher extinction coefficient per ion.

With a lesser degree of Fe^{3+} -ion absorption, as in the case of 0.5 mm thick samples in Fig. 6, the predominant feature of the curve is level region between 0.40 and 0.42 μm . For this reason the ratio of the absorption at 0.41 vs the absorption at the wavelength of maximum transmission (typically about 0.550 μm) is taken as an indication of the total Fe^{3+} -ion concentration in the glass.

The Ligand field theory also predicts a single absorption band for Fe^{2+} -ions in octahedral symmetry which is observed at

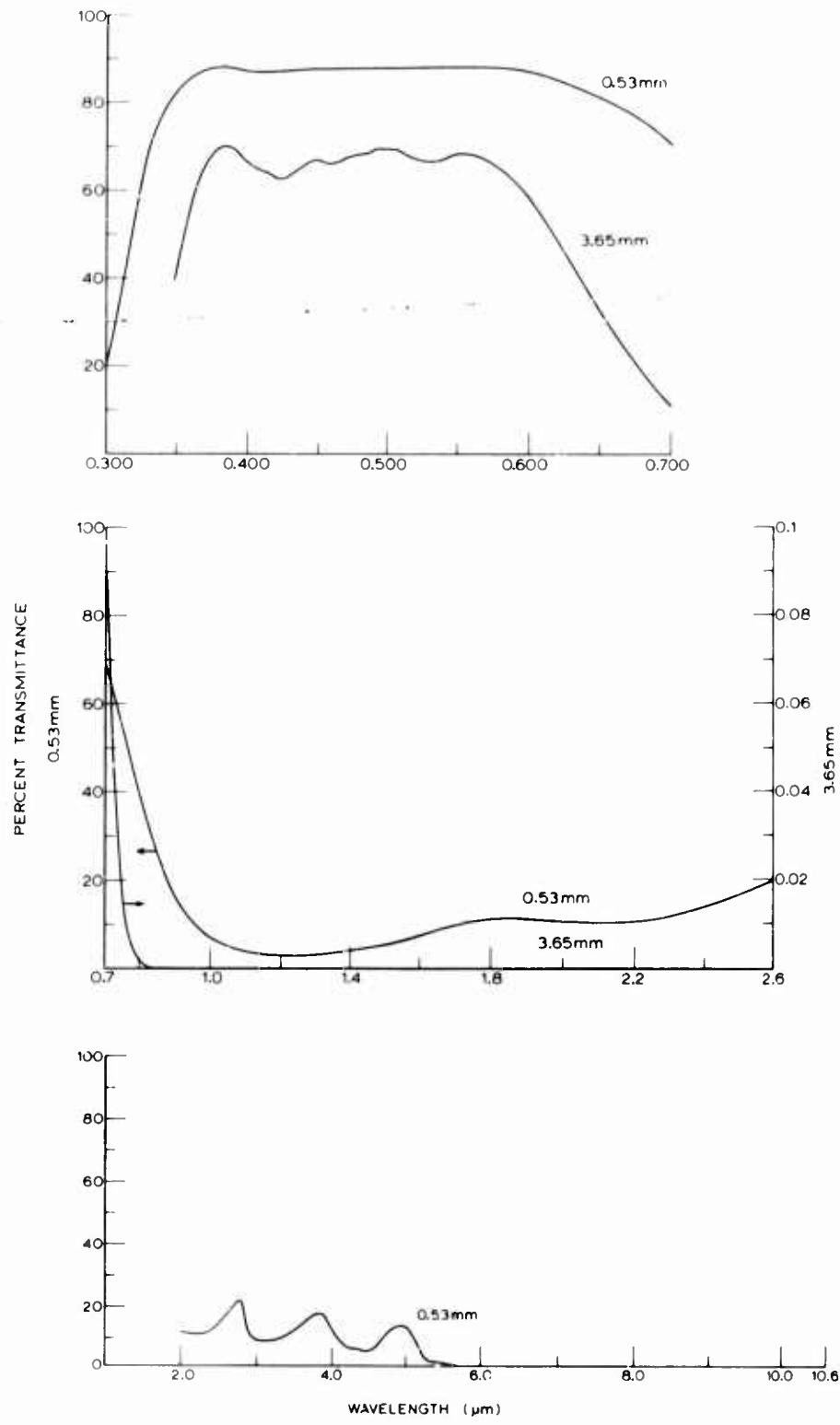


Figure 6. Transmission spectra of OLF-61-K.
Sample thickness of 0.53 mm and 3.65 mm.

1.1 μm [1] in silica glass and at about 1.2 μm in the present phosphate glasses. It further predicts that if Fe^{3+} -ions existed in a tetrahedral symmetry they should absorb in the region of 2.5 μm , but that no known observation had been reported at that time. The observed absorption band located in the 2.2 to 2.3 μm region of the Fe-phosphate glasses appears to be directly proportional to the Fe^{3+} -ion concentration in the glass and is undoubtedly due to Fe^{3+} -ions in a tetrahedral site. Thus, the transmission peak (1.8 to 2.0 μm) which occurs due to the separation between these two bands is also a function of the FeO concentration in the glass and can be controlled by controlling the iron concentration.

Absorbed Gasses: As previously stated, the peak at 5 μm lies on the absorption edge of the host glass and is not a problem in maintaining an optical density of 4 or greater throughout the infrared region. This leaves only the transmission peaks at 2.75 μm and 3.75 μm as "uncontrolled" factors in maintaining an optical density of 4.

In addition to the investigation of the rare-earth oxides to provide protection at the 2.75 μm and 3.75 μm wavelengths, a study was also made of the addition of absorbed gasses to the glass structure to provide absorption at these wavelengths. Although a wide variety of melt conditions were used on various glass compositions, the initial experiments for a given melt condition were, in general, first carried out on a single composition, OLF-1, in order that valid comparison of results could be made.

A summary of some of the results obtained in this study is given in Table VI. The goal here was to provide additional absorption at the above two infrared wavelengths while maintaining a reducing condition in the melt to keep the iron in an Fe^{3+} valence. The carbonates and sulfates were investigated as possible additional absorption bands. Chlorine was investigated in an attempt to change the Ligand field strength by substituting chlorine ions for some of the oxygen ions surrounding the Fe^{3+} -ions in hopes of broadening the absorption band on its long wavelength side to provide additional absorption at 2.75 μm .

The general conclusion of this study is that the peak at 2.75 μm is due to the overlap of the long wavelength tail of the Fe^{3+} absorption band and the onset of the OH^- -absorption band. To increase the absorption in this region one therefore needs to maintain a reasonable OH^- -absorption band and increase the long wavelength tail of the Fe^{3+} absorption band by increasing the concentration of FeO in the glass.

Table VI. Effect of absorbed gasses on transmission spectra of Fe-glasses.

Melt Number	Melt Conditions	Transmission (λ) vs wavelength (μm)						Thickness (mm)
		410	Max ^a	1.06	2.75 ^b	3.0 ^c	3.75 ^b	
OLF-1	Air atmosphere	82	86	22.5	40	18	27	18
OLF-1A	Zn and Fe added as chlorides	76.2	84.5	27.8	49	35	44	27.5
OLF-1B	Zn added as carbonate and CO-CO ₂ bubbled through melt	78	83.5	24.0	49	46	55	30
OLF-1C	Zn added as sulphate and SO ₂ bubbled through melt	69	80	33	55.5	51	57	29
OLF-1D	Zn added as ZnCl ₂ , sugar, and N ₂ atmosphere	88.8	90	16	39	37	46	26
OLF-1E	P ₂ O ₅ added as H ₃ PO ₄ , N ₂ atmosphere	66.5	78.5	45.3	65	50	57	30
OLF-1F	Sugar, N ₂ atmosphere	89.2	90	18.5	40	31	41	24
OLF-1G	N ₂ and H ₂ O vapor bubbled through melt	70	79.5	35	54	33	43	27
OLF-1P	N ₂ and H ₂ O vapor atmosphere	89.8	90	17	36.5	23	32	20

^aPeak transmission in the visible region.

^bTransmission peaks in the IR.

^cAbsorption band due to water.

The transmission peak at 3.75 μm results from insufficient overlap between the long wavelength tail of the OH⁻-absorption band and a fundamental absorption of the host glass material. Decreasing the transmission at this wavelength can therefore be accomplished by increasing the water content of the composition.

Small experimental 100 to 200 gram melts were used to determine what properties of the melt conditions were required in order to achieve the desired spectral characteristics of the glass. Determination of the specific melt conditions to be used was delayed until "production" sized melts (5 kg to 7 kg) were in progress because reducing conditions within the melt, volatilization due to time-temperature cycles etc., are strongly dependent on melt size.

V. HARDWARE PRODUCTION

The first step in the production of deliverable items under this contract was to scale-up the size of the glass melts from the small 100-200 gram size to a 5-7 kg size melt, which is more economical for the production of the quantities of raw material required. The composition chosen for the initial 5 kg melts, OLF-50, was a modification of OLF-36 which was chosen based on the results of the series of glasses in which the relative concentrations of ZnO, Al₂O₃ and P₂O₅ were investigated, taking into consideration both the spectral properties of the resulting glass and the degree of difficulty encountered in making the glass. Three melts were made with varying degrees of reducing conditions to gain some experience in the melting and casting characteristics of these larger sized melts. Transmission data on these glasses indicate that good Fe²⁺:Fe³⁺ ratios are attainable in these large melts, but that a higher concentration of FeO is required to provide adequate absorption at 2.75 μm . Some melting problems were encountered due to a surface scum which formed on the melts containing higher concentrations of reducing agent in the batch.

Initial attempts to increase the FeO concentration (OLF-55, 6 wt% FeO) resulted in an increase in Fe³⁺-ion absorption in the glass. Increasing the reducing conditions in the glass through the addition of sugar to the batch composition accentuated the problem of scum formation on the top of the melt. Additional 5 kg melts were made of compositions with intermediate concentrations of FeO, namely, OLF-60 (4 wt% FeO) and OLF-61 (5 wt% FeO) in an attempt to reach a compromise between: (1) Fe³⁺ ion formation, (2) sufficient FeO concentration to provide absorption at 2.75 μm , (3) absence of scum formation on the top of the melt, and, (4) sufficient water content to provide absorption at 3.75 μm .

The scum formation introduces problems in homogenizing the melt, which is usually accomplished by stirring, and in pouring of the molten glass from the crucible onto the casting table. Mixing scum into the glass in either process results in opaque flakes and striae in the finished product. Results indicated, however, that a heavy scum appears to serve as a barrier at the interface between the molten glass and the atmosphere which retains a reducing, OH^- -rich atmosphere within the melt. The best compromise seemed to be obtained in the OLF-61 composition and this composition was therefore chosen as the material to be used in the deliverable hardware items.

In an effort to maintain the desirable action of the scum without the disadvantages it introduces in the casting and stirring processes, experimental melts were made, again using composition OLF-1, in which moisture-rich nitrogen was either bubbled through the melt (OLF-1-O) or introduced just above the melt to form a mantle of moisture-rich nitrogen gas (OLF-1-P). Results on the 100 gram melts (Table VI) were encouraging and this technique was scaled-up and applied to 5 kg melts of OLF-61.

Results on these larger melts indicated that a higher degree of reduction was required. To accomplish this the nitrogen gas was replaced by a mixture of 5% hydrogen - 95% nitrogen. This technique appears to work satisfactorily and was used on subsequent melts. Transmission of 0.5 mm samples of this material indicates that the desired optical density of 4 can be achieved in a sample thickness of about 3.5-3.6 mm.

The validity of this extrapolation process may be checked by reference to Fig. 6 where transmission curves of a nominal 0.5 mm (0.53 mm) and a 3.65 mm thick sample of OLF-61K were given. The near IR was measured for both samples on a Cary Model C-14 spectrophotometer. For the thicker sample, a neutral filter of OD-2 was used as a reference and the sensitivity was set at 10 \times so that an effective sensitivity of 1000 \times was available out to 2 μm or more. Data extrapolated from the 0.53 mm curve indicate that a sample thickness of 3.33 mm is required to provide an OD of 4 at the peak transmission of 22% at 2.75 μm . Since the Cary is intensity limited beyond about 2 μm the optical density at 2.75 μm of the 3.65 mm sample in Fig. 6 cannot be checked directly, however, the 0.53 mm sample also has a transmittance of 22% at about 0.870 μm . When a comparison is made at this wavelength, the 3.65 mm sample has an optical density of 4.3 in good agreement with the predicted value of 4.0 for a 3.33 mm thick sample, i.e. 1.18 OD/mm vs 1.20 OD/mm, respectively.

The Federal Drug Administration's statement of General Policy which went into effect January 1, 1972 requires that all eyeglasses be treated for "improved impact resistance." This was achieved on lenses made from the OLF-61 material by the traditional heat-treatment tempering process. A heat-treatment cycle was established for this material which differs from the conventional ophthalmic materials in that it is a phosphate-based glass rather than a silicate-based glass and also has heat absorption properties markedly different from standard ophthalmic materials. Because of the lens thickness required to achieve an optical density of 4, the tempering treatment resulted in a lens which passed the standard "drop ball" test requirements for "safety" lenses. These glasses were not designed to be safety goggles, however, and it is not recommended that they be used as such.

In order to control the optical density of the goggles, each of the thirteen production melts that were made of the OLF-61 composition had a transmission measurement made on a nominal 0.5 mm thick sample. From this information the thickness required for an optical density of 4 was calculated for each melt. The melt history of each lens was maintained throughout its manufacturing process and the thickness of the finished lens was checked against the required thickness calculated for the parent melt before the lens was mounted in a frame.

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